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# Thermal Conductivity of Pristine and Brominated P-100 Fibers



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# THERMAL CONDUCTIVITY OF PRISTINE AND BROMINATED P-100 FIBERS

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## ABSTRACT

Thermal conductivity of brominated and pristine Union Carbide P-100 graphite fibers in the 30 to 160 °C temperature range was determined by measuring thermal conductivities of graphite fiber epoxy composite samples and then excluding the epoxy contribution. A comparative thermal conductivity instrument was used to measure the thermal conductivity of the samples containing fibers. Results showed that the thermal conductivity values were 225 to 370 W/m-K and 215 to 340 W/m-K for pristine and brominated fibers, respectively. Furthermore, the thermal conductivity ratio of brominated to pristine P-100 fibers was 0.89, 0.91, and 0.92 at 55 to 80 °C; 108 and 130 °C respectively. Such decrease in thermal conductivity is resulted almost entirely from the 10 percent increase in fiber cross-sectional area due to bromination. This result suggested that bromination effects on P-100 fiber structure is small, and that some structural changes, presumably the sharp-angled domain wall becomes less sharp, occurred in the 80 to 108 °C temperature range.

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## INTRODUCTION

Bromination of pitch based P-100 fibers from Union Carbide Corporation results in changes of the fiber's physical properties. It has been reported

that after bromination of these fibers, the electrical conductivity increases by about five times (Ref. 1), the mass increases by about 18 percent (Ref. 2), and the fiber diameters increases by about 5 percent (Ref. 1). Furthermore, the fiber surfaces contain very little if any bromine (Ref. 3). This new fiber is believed to be useful as a shielding material to protect electronic instruments from electromagnetic interference or as a conductive material in composites to improve composite aircraft tolerance to lightning strikes.

Another potential application of these brominated fibers is brominated P-100 epoxy composite material heaters for deicing airplane surfaces or helicopter rotors. The electrical resistivity of such composite material in the direction of the uniaxial fibers is 90 $\mu\Omega$cm if the fiber volume fraction is 60 percent. This resistivity value is about the same as that of a typical chrome-nickel heating element. In order to know how uniformly and how fast heat can be transferred from such heaters to the items being heated, the thermal conductivities of this composite material in both fiber direction and transverse direction must be determined. This report describes the efforts of measuring and computing the thermal conductivity of such a composite material in the fiber direction. The value thus obtained was used to calculate thermal conductivity of the fibers in this composite material.

In addition to measuring the thermal conductivities of pristine and brominated P-100 fibers, this report also describes a method to use very limited supply of fibers (i.e., 0.1 gm of fibers) to estimate its thermal conductivity. Theoretical implication of the thermal conductivity data on the structural damages during the bromination process will also be discussed.

## APPARATUS AND PROCEDURE

The comparative thermal conductivity measurement instrument, the samples of unknown thermal conductivity, and the equations used to calculate thermal

conductivity values from the data obtained from experiments are described below.

## Instrument

The instrument used to measure thermal conductivity of unknown samples was the Model TCFCM comparative thermal conductivity instrument manufactured by Dynatech Corporation. A schematic diagram of this instrument is shown in Fig. 1. The instrument has a central part thermal column shown in Fig. 2. It consists of a pressure pad, a main heater, a top reference standard, a sample, a bottom reference standard, an auxiliary heater, a heat sink, and spacers. The compressive pressure in the thermal column was controlled to ensure uniform thermal contact between the reference materials and the sample. Spacers were used to adjust the height so that the two standards and the sample are centered with respect to an outside thermal guard. Temperature of the outside guard was also controlled in order to minimize the temperature gradient in the horizontal direction. During operation, the space between the outside guard and the thermal column was filled with diatomaceous sillica ("Celite" made by Manville) to act as a thermally insulating powder in order to ensure one-dimensional heat transfer parallel to the thermal column direction. According to the manufacturer, the thermal conductivity of this thermal insulating powder is 0.07 W/m-K at 100 °C.

The thermal column and the outside guard were placed in a vacuum bell jar. Temperatures at points 1 to 6 were measured by type K thermocouples. The cross-sectional area and shape of the two references and the sample were the same in order to ensure one-dimensional heat flow. By applying proper control on the main heater and auxiliary heater, steady state, one-dimensional heat transfer from top to bottom of the thermal column could be achieved. In this case, the heat transfer rate, Q, would be

$$Q = \frac{\left[\frac{k_{rt}A(T_1 - T_2)}{\Delta x_t}\right] + \left[\frac{k_{rb}A(T_5 - T_6)}{\Delta x_b}\right]}{2} \quad (1)$$

where $T_1$, $T_2$, $T_5$, and $T_6$ are temperatures at points 1, 2, 5, and 6, respectively (see Fig. 1); $\Delta x_t$ is the distance between points 1 and 2; $\Delta x_b$ is the distance between points 5 and 6; A is cross-sectional area; and k is the thermal conductivity. The subscripts rt, and rb represent top and bottom reference materials, respectively.

The thermal conductivity of the sample can be calculated from the following formula:

$$k_s = \frac{Q\ \Delta x_s}{A(T_3 - T_4)} \quad (2)$$

where $k_s$ is the thermal conductivity of the unknown sample, $T_3$ and $T_4$ are temperature at points 3 and 4, respectively, and $\Delta x_s$ is the distance between points 3 and 4.

## Samples

Two different kinds of samples were used in the experiments: samples containing a small number of strands of fibers for an order-of-magnitude estimation of a fiber's thermal conductivity, and samples containing a large volume fraction of fibers typical of a graphite-eqoxy composite for a more accurate determination of thermal conductivity. In both cases the samples were unidirectional composites made from P-100 graphite fibers and epoxy, with the fiber direction parallel to that of the heat flow.

The amount of heat flow through the samples can be divided into a fiber component and an epoxy component, as described by the following equations:

$$Q = \frac{k_s A(T_3 - T_4)}{\Delta x_s} = \frac{k_f A_f(T_3 - T_4)}{\Delta x_s} + \frac{k_e A_e(T_3 - T_4)}{\Delta x_s} \quad (3)$$

where subscripts f and e represent fibers and epoxy, respectively. Rearranging the above equations give the thermal conductivity of the fiber

$$k_f = \frac{(k_s A - k_e A_e)}{A_f} \tag{4}$$

The two kinds of samples are described as follows:

(1) Nine (or sixteen) strands of fibers were embedded in a cylindrical-shaped epoxy to form the 1-in. diameter sample. The fibers were axially directed and were exposed to the outside at both ends of the cylinder. The position of the fibers is described in Fig. 3. The samples were made by forming a 1-in. diameter, cured epoxy cylinder, drilling 9 or 16 holes in axial direction through the cylinder, placing the fibers in the holes, filling the holes with epoxy, and finally curing the epoxy and refinishing both ends. The epoxy resin used in this experiment was Model 301-2 from Epoxy Technology Corporation. It has an 80 °C curing temperature, a 2 hr curing time and a 1 day potting life. It was cured in a mold made of 1-in. schedule 40 copper pipe with 1-in. inside diameter and with one end plugged by a rubber stopper. The cured product was transparent so that the fibers in this cylindrical epoxy can be seen clearly.

Since the 9 or 16 strands of fibers (about 0.15 $mm^2$ per strand) had cross sections much smaller than the cross section of the sample (about 507 $mm^2$), A and $A_e$ in Eq. (4) were considered to be the same. Thus, Eq. (4) became

$$k_f = (k_s - k_e)\left(\frac{A}{A_f}\right) \tag{5}$$

The values of $k_s$ and $k_e$, thermal conductivities of epoxy embedded with 9 or 16 strands of fibers and that of pure epoxy, respectively, can be measured by the instrument described above. Knowing the cross section was

507 $mm^2$ in diameter of the sample and 0.15 $mm^2$ for one strand of fibers, thermal conductivity of the fibers could be calculated.

The equations derived here are based on the assumption that any cross-sectional area of the thermal column is an isothermal surface. This assumption comes into question in the fiber-strands-in-epoxy cases described here because of the nonuniform structure of the cross-sectional areas of the sample. In order to alleviate this problem, two copper disks (2.54 cm diam and 0.79 mm thick) were placed between the two reference materials and the sample to ensure isothermal surfaces at both ends of the sample (see Fig. 1).

(2) Unidirectional graphite fibers-epoxy composite material, with fiber's volume fraction in the composite predetermined and fibers in heat flow direction, was used as the second kind of sample. The epoxy used for these samples was Ciba Geigy's MY720 and 976 DDS hardener. From Eq. (4), knowing that the thermal conductivity of the graphite fibers was much larger than that of epoxy ($k_f/k_e$ approximately 1000) and that the fiber's volume fraction of the composite was in the 0.5 to 0.7 range, the second term of this equation can be neglected. The resultant equation is

$$k_f = \frac{k_s}{\frac{A_f}{A}} = \frac{k_s}{R} \tag{6}$$

where R is the fiber's volume fraction in the composite.
The description of individual samples, their dimensions, filler ratios, and the reference materials used for the experiments are summarized in Table I.

Thermal Conductivity Ratio of Brominated to Pristine P-100 Fibers

The thermal conductivity ratio of brominated to pristine P-100 fibers was obtained first by measuring the individual thermal conductivities and then calculating their ratio. A second and more accurate method was also used to estimate this ratio. This method involved using a thermal column consisting

of pristine P-100 epoxy composites as the reference material and brominated P-100 epoxy as the unknown sample. Rearranging Eqs. (1) and (2), and letting $k_{rt} = k_{rb} = k_r$, $\Delta x_t = \Delta x_b = \Delta x_r$, $T_1 - T_2 = \Delta T_t$, $T_3 - T_4 = \Delta T_s$, and $T_5 - T_6 = \Delta T_b$ one has

$$\frac{k_s}{k_r} = \frac{(\Delta T_t + \Delta T_b)\Delta x_s}{2\ \Delta T_s \Delta x_r} \tag{7}$$

In this particular case, $k_s$ and $k_r$ are the thermal conductivities of brominated and pristine P-100 epoxy composites, respectively, $\Delta T_t$, $\Delta T_b$, and $\Delta T_s$ are temperature differences measured in the top pristine composite, bottom pristine composite and brominated composite, respectively, and $\Delta x_s$ and $\Delta x_r$ are the distances between the two thermocouples in the brominated composite and the pristine composites; respectively. From Eq. (6), one has

$$k_{fs} = \frac{k_s}{R_s}$$
$$k_{fr} = \frac{k_r}{R_r} \tag{8}$$

where $k_{fs}$ and $k_{fr}$ are thermal conductivities of brominated and pristine P-100 fibers, respectively, and $R_s$ and $R_r$ are filler ratios of brominated and pristine composite, respectively.

Combining Eqs. (7) and (8), on has

$$\frac{k_{fs}}{k_{fr}} = \left(\frac{R_r}{R_s}\right)\left(\frac{\Delta x_s}{\Delta x_r}\right)\left[\frac{\Delta T_t + \Delta T_b}{2\ \Delta T_s}\right] \tag{9}$$

## RESULTS AND DISCUSSION

Figures 4 and 5 show the thermal conductivity values obtained from various samples. The values were 225 to 370 W/m-K for pristine fibers and 215 to 340 W/m-K for pristine and brominated P-100, respectively. It is believed that the data obtained from the highly filled composite fiber samples were

most accurate since the thermal contact resistance between these samples and the reference materials was the lowest among all samples. This low thermal contact resistance resulted from the samples being adhered to the reference materials by silver paint, and the thermal column being under compressive force. The thermal conductivity of the pristine P-100 fibers agreed with that obtained by Hereman (300 W/m-K at room temperature; Ref. 4), but was somewhat lower than the value obtained by Union Carbide Corporation (520 W/m-K, Ref. 5).

Two methods were used to estimate the ratio of brominated P-100 thermal conductivity to pristine P-100 thermal conductivity. The first method was direct use of the thermal conductivity measured in this experiment and described in Figs. 4 and 5. The second method involved using a thermal column consisting of pristine P-100-epoxy composite as references and brominated P-100-epoxy composite as the unknown sample. Substituting the data obtained from this thermal column in Eq. (9), the thermal conductivity ratio was calculated. Figure 6 shows the results. It is obvious that at a temperature of 80 °C or lower, results from these two methods methods agree very well. Above 80 °C, the two methods begin to deviate from each other, with maximum deviation of about 20 percent. This deviation is believed to be due to the breakdown of the silver paint at 6061 aluminum-composite interface and the resultant poor thermal contacts of these surfaces at high temperatures in the first method. Thus, the second method is believed to be more accurate than the first method at high temperatures, and the thermal conductivity ratio of brominated to pristine fibers is in the range of 0.89 to 0.92 when the temperature was in the range of 55 to 125 °C.

By examining Fig. 6, it is obvious that the effects of bromination on thermal conductivity of P-100 fibers are small. Thus, it is concluded that the structural changes due to brominating P-100 is also small. This is especially true if one consider the fact that the 10 percent increase in fiber

cross-sectional area will result in 10 percent decrease in thermal conductivity. Therefore the thermal conductivity ratio of a single brominated graphite layer to a single pristine graphite layer is approximately 10 percent above the 0.89 to 0.92 range, or 0.98 to 1.01. In other words, the thermal conductivity of a single brominated graphite layer is about the same as the thermal conductivity of a pristine graphite layer in P-100 fibers.

The thermal conductivity ratio of brominated to pristine P-100 fibers was observed to be 0.89 when the temperature was 80 °C or lower, but increased to 0.91 and 0.92 at 108 and 130 °C, respectively. This small increase in the 80 to 108 °C range was reproduced three times and therefore apparently was not due to experimental error. Furthermore, all four points were obtained in one run. Thus, any source of error was likely to change the height, but not the shape of the curve shown in Fig. 6. This small increase in the thermal conductivity ratio in 80 to 108 °C temperature range may be explained satisfactorily if we assume that bromination of graphite fibers resulted in truely bromine intercalated compound. The sharp-angled domain wall in such compound become less sharp, and therefore more thermally conductive, when the sample temperature is above this temperature range (Ref. 6).

The equations derived here are based on the assumption that any cross section of the thermal column is an isothermal surface. This assumption comes into question in the fiber-strands-in-epoxy cases described here because of the nonuniform structure of the cross-sectional areas of the sample. But, comparing the data from highly filled composite material samples to the data from fiber-strands-in-epoxy samples (Figs. 4 and 5), the discrepancies are rarely larger than 20 percent. This suggests that using the method developed in this report, the approximate thermal conductivity of highly thermally conductive fibers with limited supplies (0.1 gm) can be obtained.

## CONCLUSION

Results of this set of experiments showed that thermal conductivities of pristine and brominated P-100 fibers were 225 to 370 W/m-K and 215 to 340 W/m-K, respectively. Upon bromination, thermal conductivity of single graphite layer in P-100 fibers remain unchanged. However, because fiber diameter increases during bromination, the thermal conductivity of P-100 fibers at 55 to 80 °C, 108 and 130 °C decreased to 89, 91, and 92 percent of its pristine values, respectively. This result suggests that some structural changes, presumably softening of the sharp-angled domain wall, occurred in the 80 to 108 °C temperature range. This result also suggests damage of P-100 fiber structure during bromination is small. Results also showed that samples from 0.1 gm fibers gave thermal conductivity values with 20 percent or smaller error. These samples could therefore be used to make order-of-magnitude estimations of thermal conductivity of fibers whose supply is limited.

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TABLE I. - SAMPLE AND REFERENCE MATERIALS USED IN THIS EXPERIMENT

| Sample number | Shape and dimension | Type of P-100 fibers | Fiber volume fraction,[d] percent | Fiber direction | Reference[a] |
|---|---|---|---|---|---|
| 1 | 1-in. diameter cylinder | Pristine | 0.27 (9 strands) | axial | Pyrex 7740 |
| 2 | 1-in. diameter cylinder | Pristine | 0.47 (16 strands) | axial | Pyrex 7740 |
| 3 | 11/16-in. cube | Pristine | 64.4 | ----- | Aluminum 6061[b] |
| 4 | 1-in. cylinder | Brominated | 0.27 (9 strands) | axial | Pyrex 7740 |
| 5 | 11/16-in. x 11/16-in. x 1-in. | ↓ | 54 | 1-in. | Inconel 718 |
| 6 | 11/16-in. cube | ↓ | 54 | ----- | Aluminum 6061[b] |
| 7 | 11/16-in. cube | ↓ | 54 | ----- | Pristine P-100[b,c] |
| 8 | 1-in. diameter cylinder | none | 0 | ----- | Pyrex 7740 |

[a]Thermal conductivity of Aluminum 6061 alloy was measured before beginning this set of experiments. The values were 151, 166, 166, and 156 W/m-K at 45.6, 86.8, 125.9, and 165.3 °C, respectively. Thermal conductivities of other references were supplied by Dynatech Corporation.

[b]For good thermal contact, silver paint was used as an adhesive to join the sample and the reference materials. Also, some compressive pressure was applied on the thermal column.

[c]A 11/16-in. x 11/16-in. x 1-in. composite with fiber in 1-in. direction and filler ratio of 64.4 percent.

[d]The filler ratio was determined from the following equation: filler ratio = $(n_c - n_e)/(n_f - n_e)$, where $n_c$, $n_f$, and $n_e$ are densities of composite fiber and epoxy, respectively. In this experiment, the densities of pristine fibers, brominated fibers, and epoxy were 2.18, 2.30, and 1.30, respectively.

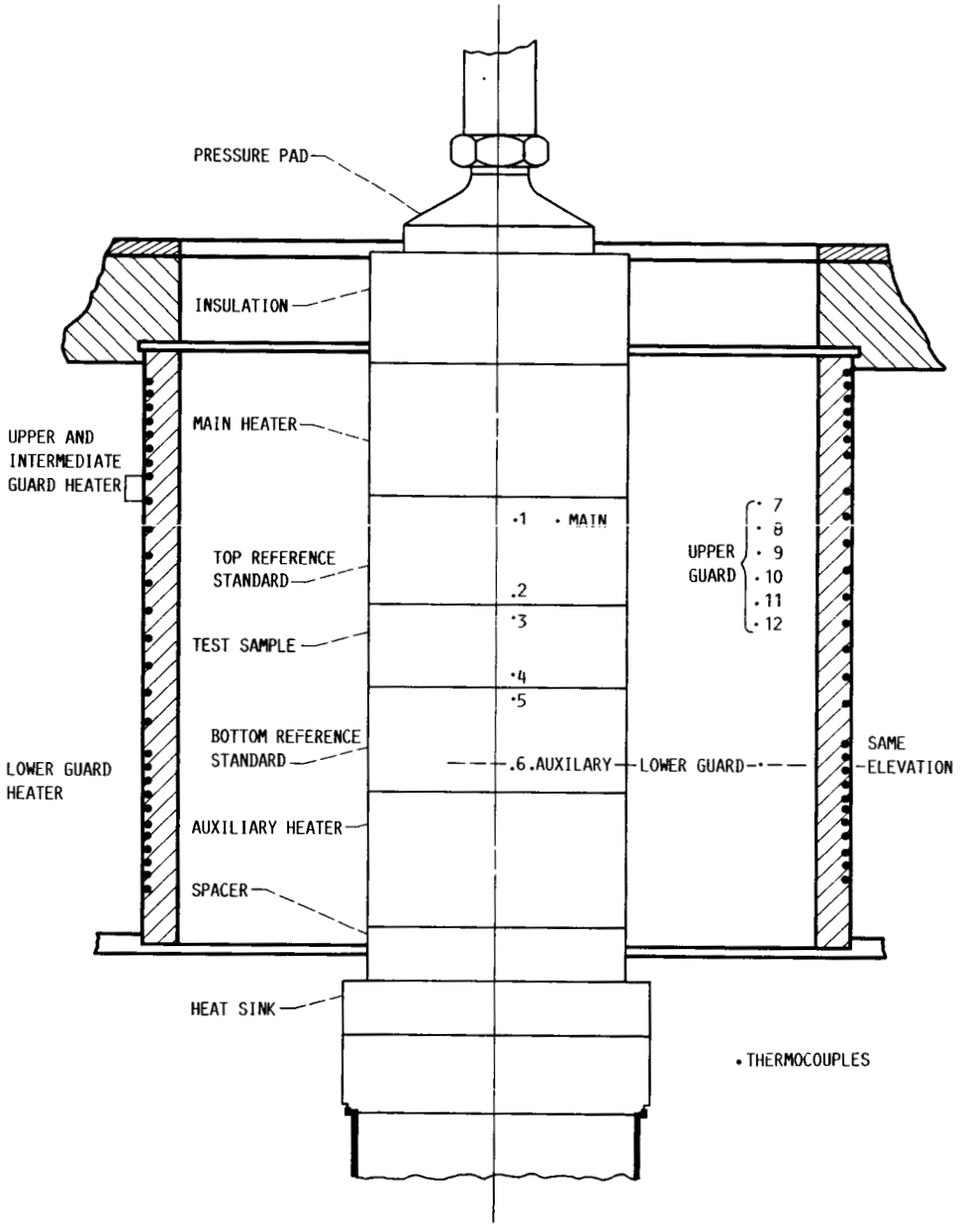


FIGURE 1.- SCHEMATIC DIAGRAM OF THE COMPARATIVE THERMAL CONDUCTIVITY INSTRUMENT.

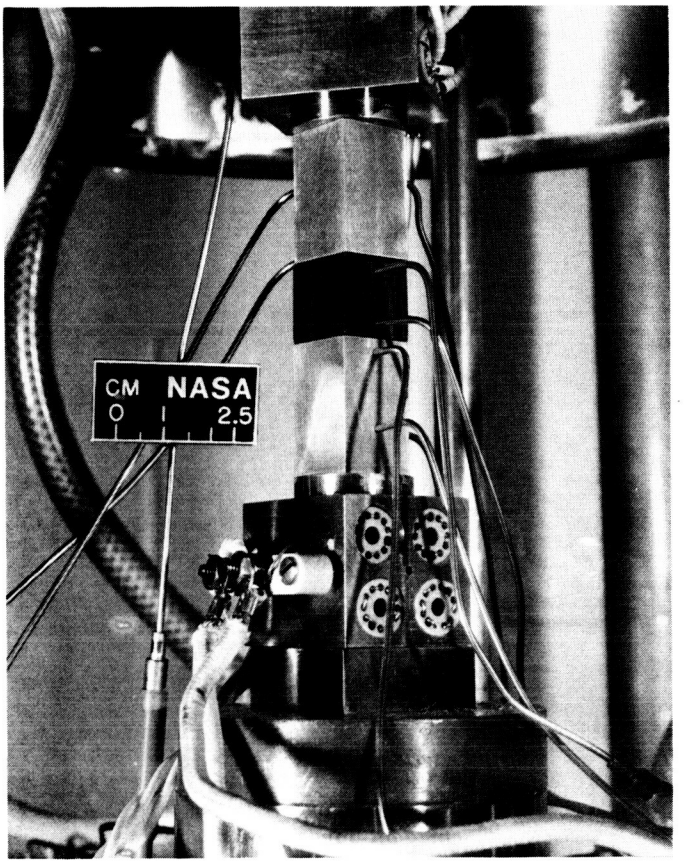


FIGURE 2.- A THERMAL COLUMN WITH THERMOCOUPLE WIRES IN THE COMPARATIVE THERMAL CONDUCTIVITY INSTRUMENT.

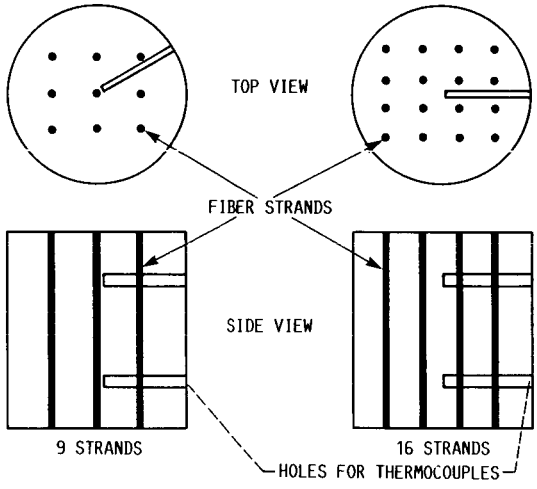


FIGURE 3.- FIBER STRANDS EMBEDDED IN 1" DIAM CYLINDRICAL EPOXY FOR THERMAL CONDUCTIVITY MEASUREMENT.

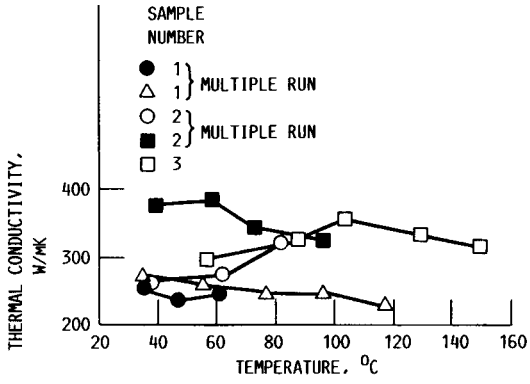


FIGURE 4.- THERMAL CONDUCTIVITY OF PRISTINE P-100 FIBER SAMPLES (THE LABELED NUMBERS ARE THE SAMPLE NUMBERS DESCRIBED IN TABLE 1).

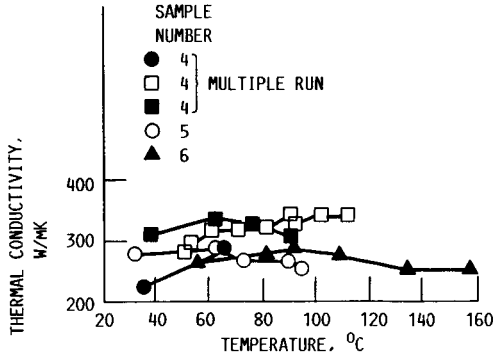


FIGURE 5.- THERMAL CONDUCTIVITY OF BROMINATED P-100 FIBER SAMPLES (THE LABELED NUMBERS ARE THE SAMPLE NUMBERS DESCRIBED IN TABLE 1).

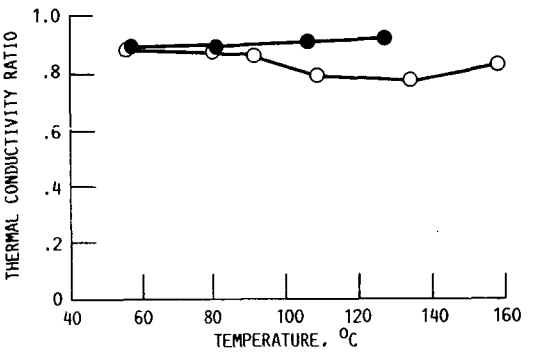


FIGURE 6.- RATIO OF BROMINATED P-100 THERMAL CONDUCTIVITY TO PRISTINE P-100 THERMAL CONDUCTIVITY. CLOSED CIRCLE: PRISTINE P-100-EPOXY COMPOSITE AS REFERENCE MATERIALS; BROMINATED P-100-EPOXY COMPOSITE AS UNKNOWN SAMPLE. OPEN CIRCLE: ALUMINUM 6061 ALLOY AS REFERENCE MATERIAL, PRISTINE AND BROMINATED P-100 AS UNKNOWN SAMPLES.

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15. Supplementary Notes

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16. Abstract

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